Nitrophenylsulfonyguaniden en hun splitsing door alkaliën

Moed, Hendrik Durk

SUMMARY.

For preparing sulphaguanidine the reaction of p-nitrobenzenesulphochloride with guanidine in alcaline medium was examined. The controversy [1]) which has arisen on the subject of this reaction has been proved to rest on incomplete examination.

The chief product in feeble alcaline solution is p-nitrobenzenesulphonyl-guanidine. Being insoluble in alcali, it may be respresented by the formula:

$$(NH_2)_2C : N . SO_2 . C_6H_4 . NO_2$$

At the same time bis-p-nitrobenzenesulphonyl-guanidine is formed. It is a rather strong monobasic acid, dissolves in alcali and gives a monosodium compound. For this and other reasons we may conclude that it possesses a SO_2NH-group and that it has this formula:

$$NH_2 . C\begin{matrix} NH . SO_2 . C_6H_4 . NO_2 \\ \diagdown\!\!\diagdown \\ N . SO_2 . C_6H_4 . NO_2 \end{matrix}$$

Examining the action of alcali on these two sulphamides, we made a curious observation. Both compounds easily loose their sulphonyl groups in the form of sulphur dioxide. The mononitro compound produces nitrophenyl-guanidine, as if the sulphonyl group was simply lifted out of the molecule:

$$(NH_2)_2C : N . SO_2 . C_6H_4 . NO_2 \rightarrow SO_2 + (NH_2)_2C : N . C_6H_4 . NO_2$$

The p-dinitro compound undergoes a more complicated decomposition:

$$NH_2 . C\begin{matrix} NH . SO_2 . C_6H_4 . NO_2 \\ \diagdown\!\!\diagdown \\ N . SO_2 . C_6H_4 . NO_2 \end{matrix} \rightarrow \begin{matrix} 2\,SO_2 \\ \\ CN . NH_2 \end{matrix} + NH(C_6H_4NO_2)_2$$

In order to know if these remarkable decompositions have a

---

[1]) Winnek obtained *p*-nitrobenzenesulphonyl-guanidine (Chem. Zentr. 1941 II, 1296), whilst Karrer reported the formation of guanidinium *p*-nitrobenzenesulphonate (Helv. Chim. Acta **24**, 310 (1941).

general character, the reactions of o- and m-nitrophenylsulphonylchloride on guanidine were examined. They gave also mononitro and dinitro derivatives.

The three mixed dinitro compounds (o m′, o p′, m p′) were obtained by interaction of the mononitro compounds with the desired nitrobenzenesulphonylchloride.

For all these compounds (3 mononitro, 3 simple dinitro and 3 mixed dinitro compounds) the action of dilute alcali was examined. The following conditions for the formation of SO_2 were stated.

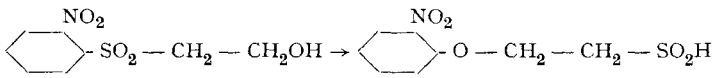
1. The presence of a nitro group in ortho or para position is required. The m-nitro and m, m′-dinitro compounds do not react. A dinitro compound with one m- and one o- or p-nitro group looses one molecule sulphur dioxide only.

2. The amino compounds, obtained by reduction of the active nitro compounds, are stable towards alcali.

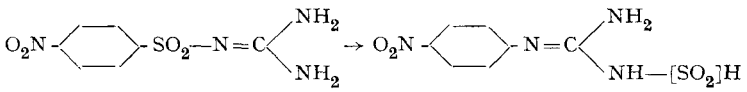
3. The presence of a NH_2 (or NH) group in the position 1—4 with regard to the SO_2 group is required. Thus following compounds are stable:

$\{(CH_3)_2N\}_2C : N . SO_2 . C_6H_4 . NO_2$ (p) $\qquad$ $NC . NH . SO_2 . C_6H_4 . NO_2$ (p)

These conditions resemble the rules for the isomerisation of aromatic hydroxy- and amino-sulphones and related compounds, studied by S. Smiles and his collaborators in many interesting publications during the years 1930—1940. A characteristic example is given by o-nitrophenylsulphonylaethanol; when heated with alcoholic soda, it isomerises to a sulphinic acid [1]):



The aromatic rest and the hydrogene of the hydroxyl group interchange their positions. If p-nitrophenylsulphonyl-guanidine undergoes a similar isomerisation, the primary product should be an amino (or imino) sulphinic acid, which is unstable and splits directly into sulphur dioxide and p-nitrophenyl-guanidine:

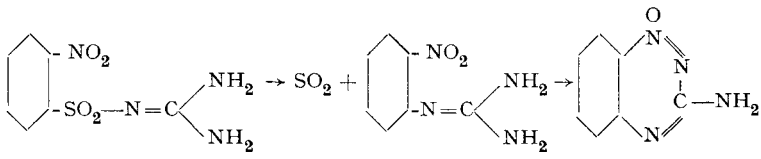


The isomeric o-nitrophenylsulphonyl-guanidine gives also sulphur

---

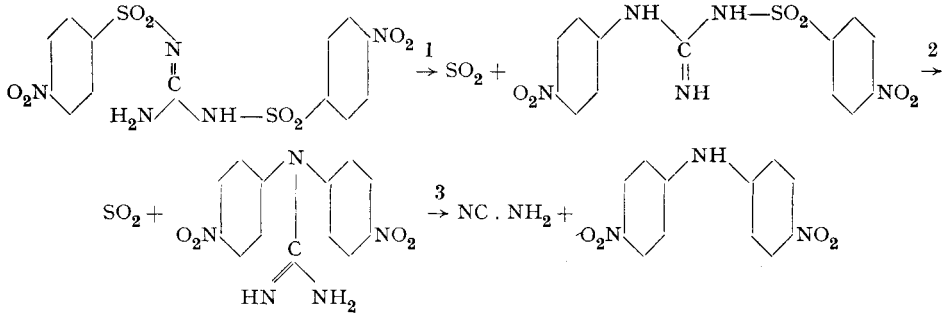
[1]) A. Kent and S. Smiles, J. Chem. Soc. **1934**, 422.

dioxide, but in stead of the expected o-nitrophenylguanidine its cyclisation product, 1-oxo-3-amino-benzo-1, 2, 4-triazine is obtained in nearly quantitative yield:



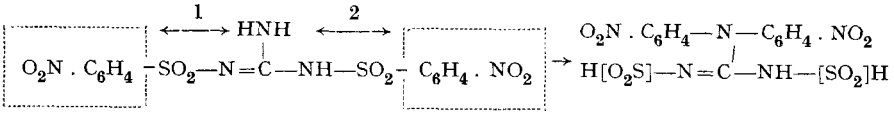
The nitrophenylsulphonyl derivatives of asymmetric dimethyl-guanidine react in the same way as those of guanidine. But the derivatives of symmetric tetramethylguanidine are perfectly stable under the same conditions. The fact, that one of the amino groups must contain at least one hydrogene atom (condition 3) is a strong argument for the isomerisation theory.

The decomposition of the bis-nitrophenylsulphonyl-guanidines is far more complicated. As a meta-nitro group does not activate the side chain, the m, m'-dinitro derivative must be stable. But the o- and p-bis-nitrophenylsulphonyl-guanidines will undergo a double decomposition. The end products are dinitrodiphenylamine, cyanamide and sulphur dioxide (2 mol.). The following scheme gives an explanation of the decomposition.



A transformation in two phases (1 and 2) is supposed, because only the first phase can be realized in the case of the o, m'- and p, m'-dinitro compounds, where the m-nitrophenylsulphonyl group is inactive. Both intermediate compounds have been synthesized; they give the same end products, cyanamide and dinitrodiphenyl-amine.

The following scheme represents in a simple way the interchange of places between the nitrophenyl group and the hydrogen atoms of the amino group:



Finally it may be observed, that the transformation studied in this thesis furnishes a practical method for preparing o- and p-nitrophenylguanidines (as II, IV, XXIX), for it is much easier to introduce in guanidines a nitrophenylsulphonyl group than a nitrophenyl group.

For the preparation of nitrated diphenylamines (as XVI, XX, XXII) the transformation also affords a very convenient method.

LIST OF NEW COMPOUNDS.

A. *New compounds.*

		p.
$C_7H_7O_2N_4Ag$	Silver salt of p-nitrophenylguanidine	73
$C_7H_8O_4N_4S$	o-Nitrophenylsulphonylguanidine, m.p. 205—206°(d)	44
$C_7H_8O_4N_4S$	m-Nitrophenylsulphonylguanidine, m.p. 199—200°(d)	42
$C_7H_9O_5N_5$	Nitrate of p-nitrophenylguanidine, m.p. 219—220°(d)	73
$C_7H_9O_2N_4Cl$	Hydrochloride of nitrophenylguanidine, m.p. 290—293°(d)	73
$C_9H_{10}ON_4$	1-Oxo-3-dimethylamino-benzo-1, 2, 4-triazine, m.p. 161—161.5°	79
$C_9H_{12}O_2N_4$	N-p-Nitrophenyl-N′, N′-dimethylguanidine, m.p. 142.5—143.5°	77
$C_9H_{12}O_4N_4S$	o-Nitrophenylsulphonyl-as.dimethylguanidine, m.p. 148—150°(d)	59
$C_9H_{12}O_4N_4S$	p-Nitrophenylsulphonyl-as.dimethylguanidine, m.p. 197—198°(d)	56
$C_{11}H_{16}O_4N_4S$	p-Nitrophenylsulphonyl-s.tetramethylguanidine m.p. 141.5—142.5°	60
$C_{12}H_9O_6N_3S$	p-Nitrophenylsulphonyl-p-nitrophenylamine, m.p. 175.5—176.5°	29
$C_{13}H_{12}O_7N_6$	Nitrate of bis-p-nitrophenylguanidine, m.p. 244°	25
$C_{13}H_{11}O_6N_5S$	N-p-Nitrophenylsulphonyl-N′-p-nitrophenylguanidine, m.p. 180°(d)	62
$C_{13}H_{11}O_6N_5S$	N-m-Nitrophenylsulphonyl-N′-p-nitrophenylguanidine, m.p. 208—210.5°	65
$C_{13}H_{11}O_6N_5S$	N-m-Nitrophenylsulphonyl-N′-o-nitrophenylguanidine, m.p. 218—222°	90
$C_{13}H_{11}O_8N_5S_2$	N, N′-Bis-p-nitrophenylsulphonylguanidine, m.p. 270—272°	37
$C_{13}H_{10}O_8N_5S_2Na$	Sodium salt of —	39
$C_{13}H_{10}O_8N_5S_2K$	Potassium salt of —	40
$C_{13}H_{14}O_8N_6S_2$	Ammonium salt of —	40
$C_{14}H_{16}O_8N_8S_2$	Guanidonium salt of —	40